UNPUBLISHED PRELIMINARY DATA

NATIONAL BUREAU OF STANDARDS REPORT

8631

QUARTERLY STATUS REPORT FOR THE QUARTER ENDING 1/31/65

ON

THE MECHANISM OF STRESS CORROSION OF TITANIUM ALLOYS
EXPOSED TO SODIUM CHLORIDE AT ELEVATED TEMPERATURES

by

Hugh L. Logan
Michael J. McBee
and
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for

Headquarters
National Aeronautics and Space Administration
Requisition No. PR10-2081
May 4, 1964
Contract No. R-130

(A PRELIMINARY REPORT; NOT FOR PUBLICATION)

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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* NBS Group, Joint Institute for Laboratory Astrophysics at the University of Colorado.
** Located at Boulder, Colorado.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT 3120448

February 3, 1965

NBS REPORT 8631

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Work has continued with the use of hollow specimens of the Ti-8Al-1Mo-1V alloy described earlier. The specimen is heated externally with a heating tape, filled with a 10% aqueous solution of 7 parts NaCl + 1 part $MgCl_2 \cdot 6H_2O$, and the solution slowly pipetted out. This leaves a layer of mixed crystals (not necessarily uniformly) on the inner surface of the specimen. The specimen is closed with a plug of the Ti-8-1-1 alloy which, however, has a 1/8 inch O.D. nickel tube extending through it so that the specimen cavity can be evacuated or a desired atmosphere introduced. The specimen is placed in a conventional creep furnace and is stressed using a modified creep apparatus.

During the report period specimens have been heated to 750°F prior to stressing and have been stressed (at temperature) to 90 percent of the yield strength at that temperature, i.e., 73,500 lb/in^2. A gas sampling tube may be connected to the specimen cavity, through the nickel tube mentioned above, so that gaseous corrosion products can be withdrawn for mass spectrographic analysis.

Specimen failures have occurred after as short an exposure period as 18 hours for a specimen containing oxygen at atmospheric pressure. The failure may be of the type shown in Fig. 1. In this case there are deformed regions on the exterior surface of the specimen (see arrows) which are due to cracking which may or may not extend entirely through the specimen wall from the interior surface. Cracks in the interior wall, noted after the specimen was split for examination, are marked by an arrow in Fig. 2. In other instances failure is complete as is seen in Fig. 3.

In early experiments specimens contained tank oxygen at atmospheric pressure. Mass spectrographic analyses of the gas content of these specimens taken prior to failure failed to reveal any evidence of chlorine. In an effort to increase the sensitivity of the test, specimens were later evacuated to a low pressure before heating, then flushed several times with tank oxygen, pumped until about 0.2 mm pressure remained in the specimen cavity and then dead loaded in tension. We have yet to obtain a completely vacuum tight specimen. We have, however, markedly increased the sensitivity of our test for chlorine. In a recent test in which no free chlorine was detected, calculations indicated that the sensitivity was such that one molecule in 10,000 of the chlorine put into the specimen cavity as sodium or magnesium chloride could have been detected had it been uncombined. Workers at the Titanium Metals Company Laboratory* reported detecting free chlorine using starch iodide paper. In preliminary tests using this method of detection in addition to our mass spectrographic analyses we have not found free chlorine.

* Private communication.

While tank oxygen is put into the specimens at a pressure of about 0.2 mm, the mass spectrographic analysis indicated that the gas content of the specimens was largely nitrogen. This indicated that the oxygen originally present had combined with the titanium and the nitrogen represented an air leak, the oxygen in the air also combining with the titanium alloy. The water vapor in this sample amounted to only 0.3% of the nitrogen. Calculations indicated that this would be only about 1/2 the amount expected in the laboratory air. As the evacuated specimen, containing a mixture of 7 parts NaCl and 1 part $MgCl_2 \cdot 6H_2O$, is heated a rise in pressure occurs in the temperature range of 350° to 450°F. This is just the range in which hydrated $MgCl_2$ is reported to loose a part of its water of crystallization. Any water of crystallization remaining above this temperature is probably so combined with the $MgCl_2$ that it will not be directly available as water for chemical reactions. The tank oxygen added to the specimen at 750°F was run through a drying material. Hence any water available for the reaction would most probably be that contained in the air leak. It would be expected to be present in the gas sample in the same proportion as in air (instead of half that amount) unless it reacts with some material in the specimen. Water could react with titanium as follows: $2H_2O + Ti \rightarrow TiO_2 + 2H_2$ but unless the hydrogen reacted immediately with the titanium it would be found in the gas analysis. This was not the case. The other possibility is that it reacts with an oxide as follows: $MO_m + 1/2n\ H_2O \rightarrow M_m(OH)_n$. This, however, is not believed to be a primary reaction. In early experiments a drop of water was deliberately put into the specimen cavity along with the NaCl + $MgCl_2$. Specimens were not evacuated and the exposure periods to failure were longer than with specimens in which dried oxygen was placed in the specimen cavity.

X-ray diffraction patterns of a thin film stripped from the interior wall of a failed specimen indicated that it was primarily anatase (TiO_2). The layer was so thin that transmission electron-micrographs could be taken through it, Fig. 4. The heavy dark portion extending diagonally across the micrograph is a region too thick for electron penetration. The spike like structures seen in the micrograph are of interest but have not been identified.

A number of sheet specimens, 0.040 inch thick of the Ti-8Al-1Mo-1V alloy, were stressed as beams by four point to 40, 60 and 80 percents of their yield strengths. They were then coated with NaCl by one of the two following methods: (a) The specimen surfaces were wet with distilled water and finely powdered NaCl was sprinkled on them; (b) an aqueous solution of NaCl was sprayed on the specimen;

it was dried, and the process was then repeated until an appreciable layer of NaCl was built up on the specimen surface. The latter method gave the better surface layer. Specimens, coated by both methods, have now been exposed in air at 750°F for about 7 weeks. No failures have occurred.

Sheet specimens of the Ti-8Al-1Mo-1V alloy and a jig for stressing them are being prepared for x-ray diffraction studies of the salt-alloy reaction in air at 700-750°F.

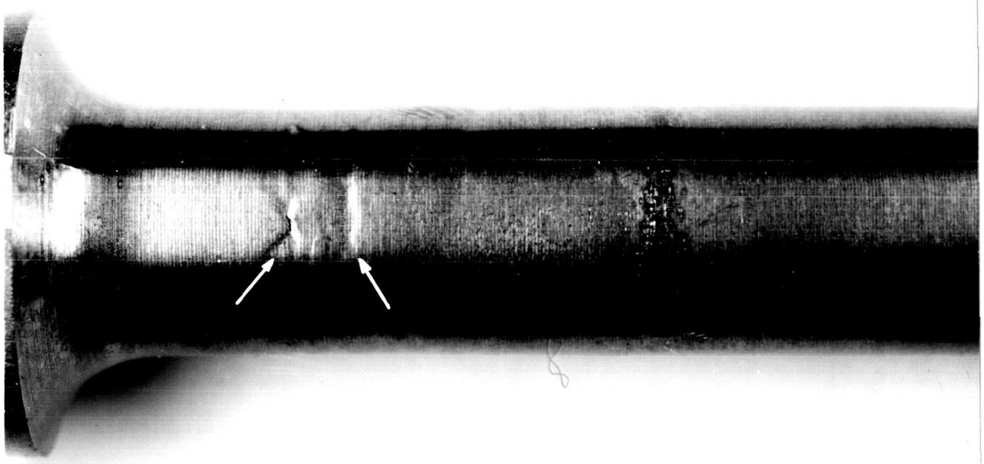

Figure 1. Exterior of specimen that had been exposed at 750°F under stress of 72,500 psi. Interior coated with NaCl + $MgCl_2 \cdot 6H_2O$. Specimen evacuated to 0.01 mm mercury pressure and tank oxygen added to pressure of 0.2 mm. Distorted areas associated with stress-corrosion cracks in interior wall of specimen. Cracks may extend entirely through specimen wall. X 2

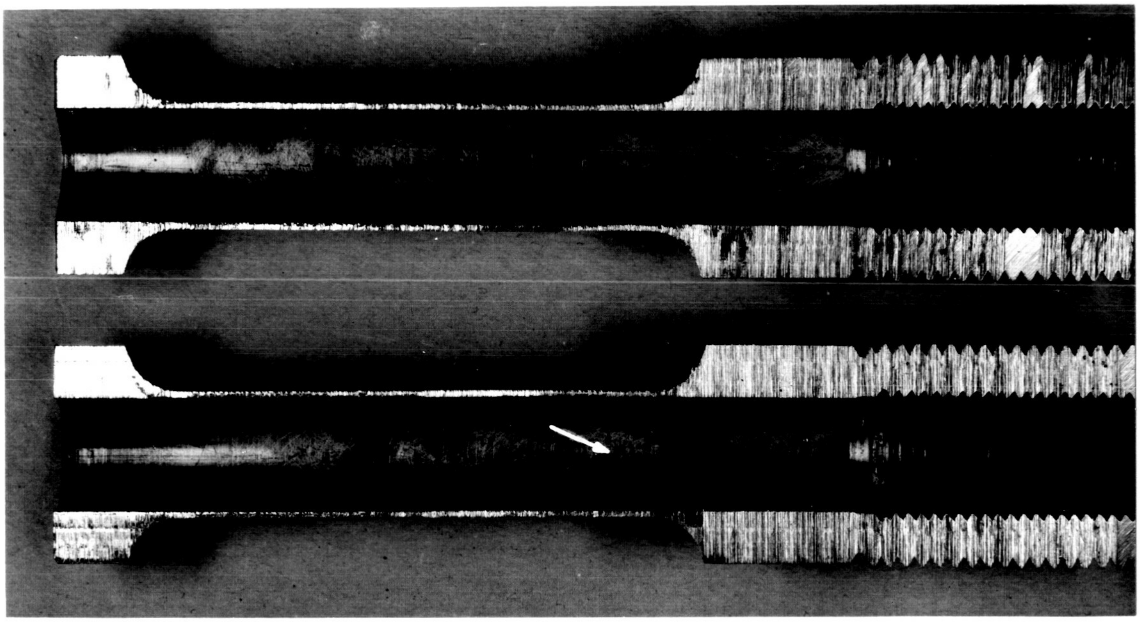

Figure 2. Specimen exposed under same conditions as that in Fig. 1 and after failure was evident split for internal examination. Cracked area is indicated by arrow. X 1-1/2

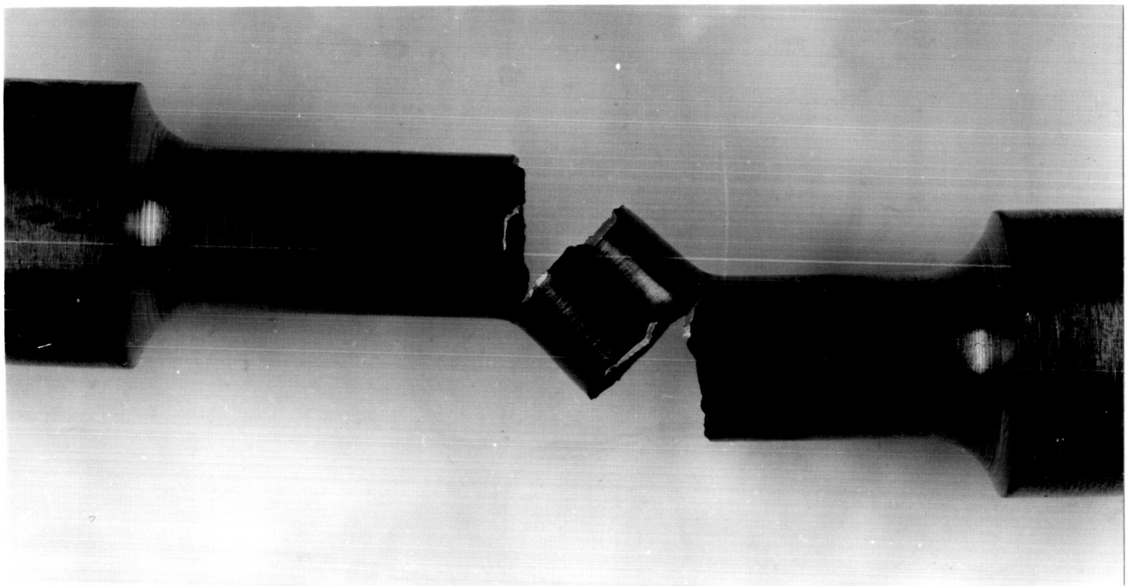

Figure 3. Complete failure of specimen containing inner coating of NaCl + $MgCl_2 \cdot 6H_2O$. Specimen exposed under stress of 72,500 psi at 750°F. Interior evacuated and oxygen added to pressure of 0.2 mm mercury. X 1-1/2

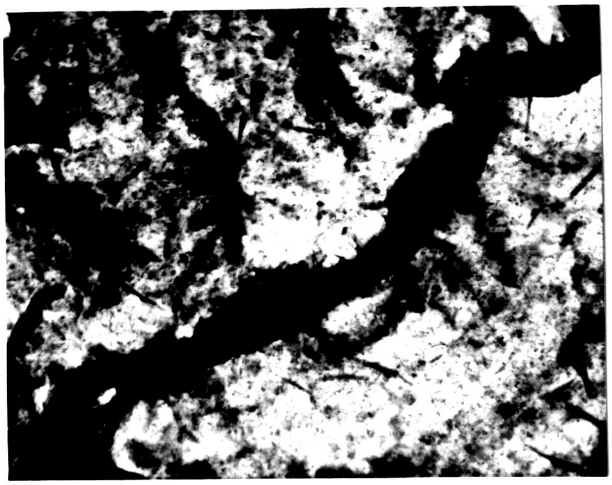

Figure 4. Electron transmission micrograph of surface film stripped from interior surface of failed specimen. Note dark spike like structures. Dark diagonal band is structure too thick to be penetrated by electron beam. X 18,000